

III.A.19 SOFC Interconnect Materials Development at PNNL

Objectives

- Develop and optimize cost-effective materials for intermediate temperature SOFC interconnect and interconnect/electrode interface contact applications.
- Develop, characterize, and validate materials degradation processes in SOFC operating environments.
- Utilize the basic understanding in the development of advanced alloys and surface coatings with adequate bulk and interface corrosion tolerance.

Accomplishments

- Compiled structural, electrical, and chemical properties of $(\text{Mn},\text{Co})_3\text{O}_4$ spinels.
- Synthesized, tested, and characterized spinel coatings on ferritic stainless steel (FSS) substrates.
- Completed the evaluation of Mn-modified Ni-base alloys under SOFC operating conditions.
- Initiated dual atmosphere oxidation tests on selected FSS alloys using simulated reformat fuel.

Introduction

With the reduction in SOFC operating temperatures, low-cost high-temperature oxidation alloys have become promising candidates to replace lanthanum chromite, a ceramic that can withstand operating temperatures in the 1000°C range. To improve the understanding of the advantages and limitations of alloy interconnects, PNNL has been engaged in systematic evaluation and development of candidate materials. Challenges to be overcome include chromia

scale evaporation, scale electrical resistivity, oxidation/corrosion under interconnect dual exposure conditions and scale adherence, and compatibility with adjacent components, such as seals, electrodes and/or electrical contact materials.

Approach

Oxidation behavior of candidate alloys is being investigated under dual atmospheres (simultaneous exposure to an oxidizing and reducing environment) conditions typical of SOFC interconnect operation conditions. Studies are being performed in both air/hydrogen/steam and air/simulated-reformat environments in the 600-800°C temperature range. Bulk modifications, as well as surface coatings, are being investigated to provide long-term oxidation resistance, mitigate Cr evaporation and facilitate electronically conducting interface formation.

Results

$(\text{Mn},\text{Co})_3\text{O}_4$ spinel coatings have been successfully fabricated onto Crofer22APU FSS substrates. Recently, spinel coatings were successfully applied to two other ferritic stainless steels, E-brite and 430, by slurry coating followed by heat treatment in a reducing environment and then oxidation in air. Figure 1 shows a scanning electron microscope (SEM) micrograph of a coated 430 sample after the initial heat treatment (reduction in $\text{Ar}/3\%\text{H}_2\text{O}/2.75\%\text{H}_2$ at 800°C). At this stage, the spinel phase was reduced into a porous mixture of Co and MnO. During subsequent oxidation in air at 800°C, the MnO and Co reacted with oxygen to re-form the spinel phases, as confirmed by x-ray diffraction (XRD) analysis. A cross-section SEM image (Figure 2) after the oxidizing heat-treatment shows that the spinel layer was well bonded to the 430 substrate via an ~1.5 µm thick scale. Some residual porosity is present in the spinel layer. The partial densification of the spinel layer from the highly porous layer of MnO and Co is attributed to a sintering process that is enhanced by the spinel formation reactions occurring during the oxidizing heat treatment. As no obvious boundary was discernible between the scale and the spinel coating, it appears that the Mn-Co spinel and the native oxide scale grown on 430 are mutually compatible. Also, energy dispersive spectroscopy (EDS) analysis on the cross-section indicated that no detectable chromium penetration into the spinel layer had occurred after 100 hours at 800°C. The same approach was also successfully used for coating of E-brite samples. As in the case for 430, the protection layer acted as an effective Cr barrier during the 100 hours of heat treatment.

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$\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel coating has been found to substantially improve the electrical behavior of simulated interconnect/cathode interfaces. In recent tests, enhanced electrical performance was also observed for the other FSS substrates when spinel coatings were applied. Figure 3 shows the contact area-specific resistance (ASR) for coated 430 and E-brite, measured as a function of time during tests in air at 800°C. The contact ASR between the coated E-brite and cathode was as low as 7 m $\Omega\cdot\text{cm}^2$ in the early stages of the test and increased only slightly with time during the 400 hours measurement. Thus, E-brite behaved similarly to Crofer22APU. In comparison, the coated 430 exhibited a higher ASR, which substantially increased over time.

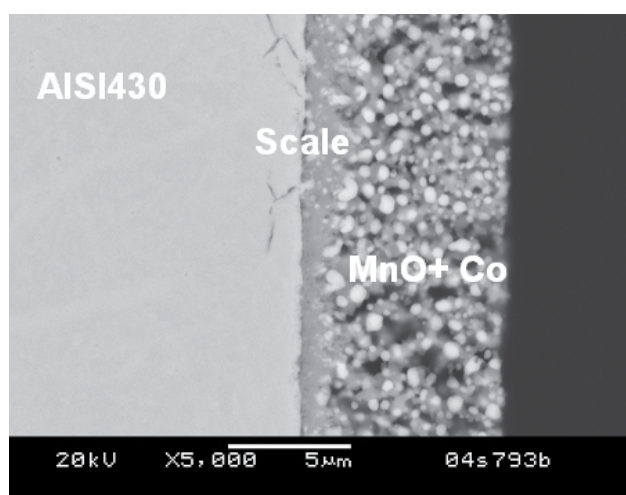


FIGURE 1. SEM Image of Cross-Section of Protection Layer on 430 Stainless Steel after Heat Treatment at 800°C in 2.75% H_2 /bal. Ar

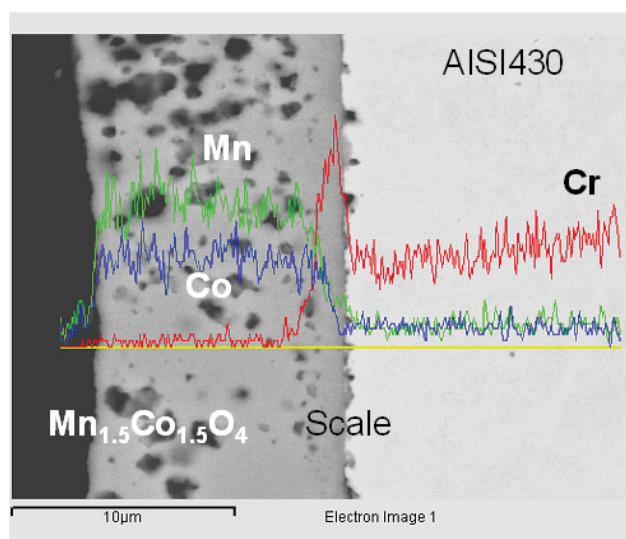


FIGURE 2. SEM Image of Cross-Section of Protection Layer on 430 Stainless Steel after Re-Oxidation at 800°C in Air

After the ASR measurements, SEM analysis on the cross-sections of the tested samples indicated that the spinel coatings were well-bonded to the ferritic substrate and free of spallation or cracks. In the case of the coated E-brite, a scale about 1.0 μm thick grew between the metal substrate and the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ coating. EDS analysis did not find evidence of Cr penetration through the spinel coating into either the contact paste or the cathode. Figure 4 shows an SEM cross-section of the coated 430. After ~ 400 hours at 800°C in air, a scale about 2.0–2.5 μm thick grew between the ferritic substrate and the coating. Both point and line EDS analyses indicated no penetration of Cr through the coating into the contact paste or the cathode. The EDS line scan did, however, find segregation of Si, likely in form of silica, at the interface between the

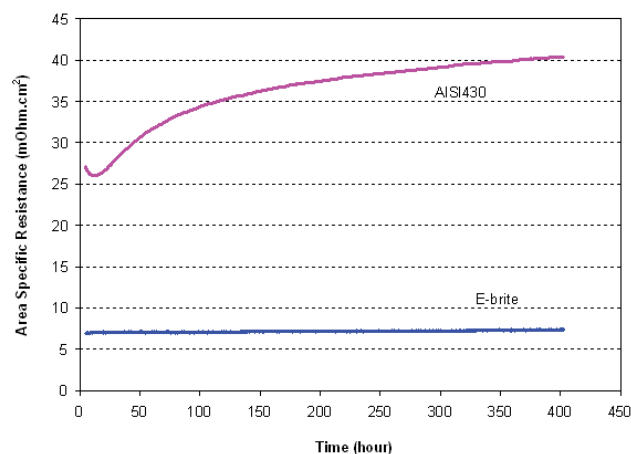


FIGURE 3. Contact ASR between LSF Cathode and a 430 or E-brite Current Collector with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ Spinel Protection Layer

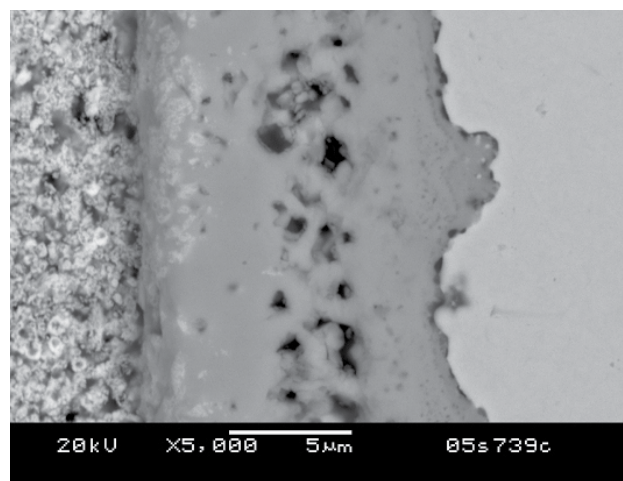


FIGURE 4. SEM Image of Cross-Section of 430 with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ Protection Layer after Contact ASR Measurement at 800°C in Air for ~ 400 Hours

scale and the metal substrate, due to residual Si in the 430 substrate. This silica layer is the likely cause of the relatively high ASR observed for the coated 430 test. Additionally, the higher growth rate of the scale beneath the spinel coating would be another contributor to the high ASR. Fe was also observed in the scale and the spinel coating, indicating Fe outward migration from the metal substrate. It is known that, with ~17% Cr, 430 forms a scale that contains Fe during high temperature exposure in air and grows faster than the scale grown on ferritic substrates with a higher Cr concentration. For example, Crofer22APU and E-brite, containing 23% and 27% Cr, respectively, exhibit a lower scale growth rate, i.e. a higher oxidation resistance, than 430. The scales grown on Crofer22APU and E-brite in air are comprised of $(\text{Mn,Cr})_3\text{O}_4$ + Cr_2O_3 and Cr_2O_3 , respectively, with negligible Fe.

Conclusions and Future Directions

- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel composition demonstrates excellent electrical conductivity, thermal and structural stability, and thermal expansion match to selected ferritic stainless steel interconnects.
- Thermally grown surface coatings of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ not only decreases the interconnect/cathode contact resistance, but also acts as (a) an anionic transport barrier to inhibit scale growth on the stainless steel and (b) barrier for the penetration of Cr through the coating.
- Future work on the development and optimization of protective coatings will focus on tailoring the spinel coating composition as well as the development of cost-effective fabrication techniques for near net shape application. Additional activities will include oxidation and corrosion tests of alloys and coatings in air/simulated reformat dual atmospheres and development of optimized contact materials for cathode/interconnect interfaces.

FY 2006 Publications/Presentations

Publications

1. Z. Yang, G.G. Xia, P. Singh, and J.W. Stevenson, "Electrical Contacts between Cathodes and Metallic Interconnects in Solid Oxide Fuel Cells," *J. Power Sources*, **155**, 246 (2006).
2. Z. Yang, G. Xia, S.P. Simner, and J.W. Stevenson, "Thermal Growth and Performance of Manganese Cobaltite Spinel Protection Layers on Ferritic Stainless Steels SOFC Interconnects," *J. Electrochem. Soc.*, **152**, A1896 (2005).

3. Z. Yang, G.-G. Xia, S.P. Simner, and J.W. Stevenson, "Ferritic Stainless Steel SOFC Interconnects with Thermally Grown $(\text{Mn,Cr})_3\text{O}_4$ Spinel Protection Layers," in *Proc. 29th International Conference on Advanced Ceramics and Composites - Advances in Solid Oxide Fuel Cells (Ceramic Engineering and Science Proceedings, Volume 26, Issue 4)*, p. 201 (2005).
4. Z. Yang, G.-G. Xia, and J.W. Stevenson, "Electrical Contacts between Cathodes and Metallic Interconnects in Solid Oxide Fuel Cells," in *Proc. 29th International Conference on Advanced Ceramics and Composites - Advances in Solid Oxide Fuel Cells (Ceramic Engineering and Science Proceedings, Volume 26, Issue 4)*, p. 217 (2005).

Presentations

1. "Conductive Protection Layers on Ferritic Stainless Steels for SOFC Interconnect Applications," Z.G. Yang, S.H. Li, G.D. Maupin, S.P. Simner, and G.G. Xia, International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, May 1-5, 2006.
2. "Development of $(\text{Mn,Cr})_3\text{O}_4$ Protection Layers on Ferritic Stainless Steels for SOFC Interconnect Applications," Z.G. Yang, G.G. Xia, G.D. Maupin, X. Li, P. Singh, J.W. Stevenson, 135th Annual TMS Meeting, San Antonio, TX, March 12-16, 2006.
3. "High Temperature Corrosion Behavior of Metals and Alloys under Influence of a Hydrogen Gradient," Z.G. Yang, G. Coffey, D.M. Paxton, P. Singh, J.W. Stevenson, and G.G. Xia, 135th Annual TMS Meeting, San Antonio, TX, March 12-16, 2006.
4. "High Temperature Corrosion Behavior of Oxidation Resistant Alloys under SOFC Interconnect Exposure Conditions," Z. Yang, G. Coffey, P. Singh, J.W. Stevenson, and G. Xia, 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 22-27, 2006.
5. "Properties of $(\text{Mn,Cr})_3\text{O}_4$ Spinel Protection Layers for SOFC Interconnects," Z. Yang, S. Li, G. D. Maupin, P. Singh, S.P. Simner, J.W. Stevenson, and G. Xia, 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 22-27, 2006.
6. "Manganese-Cobalt Mixed Spinel Oxides as Surface Modifiers for Stainless Steel Interconnects of SOFCs," G. Xia, Z. Yang, G.D. Maupin, S.P. Simner and J.W. Stevenson, 208th Meeting of The Electrochemical Society, Los Angeles, CA, October 16-21, 2005.